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## **(54) CARBON MATERIAL FOR ELECTRODE AND NONAQUEOUS SECONDARY BATTERY USING THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a carbon material for an electrode having a high electrode filling property, high energy density, and an excellent quick charging/discharging property.

SOLUTION: In this carbon material for an electrode, a surface interval (d002) by a wide angle X-ray diffraction method (002) is less than 0.337 nm, the crystallite size (Lc) is 90 nm or larger, R value which is the ratio of the peak intensity of 1360 cm<sup>-1</sup> versus the peak intensity at 1580 cm<sup>-1</sup> is 0.2 or more, and a tap density is 0.75 g/cm<sup>3</sup> or more.

## **CLAIMS**

[Claim(s)]

[Claim 1] A spacing (d002) of a field by a wide angle X-ray diffraction method (002) Less than 0.337 nm. An R value which is a peak intensity ratio of 1360 cm<sup>-1</sup> to peak intensity of 1580 cm<sup>-1</sup> [ in / in crystallite size (Lc) / not less than 90 nm and an Ar-ion-laser Raman spectrum ] 0.20 or more. And a carbon material for electrodes wherein tap density is more than 0.75 g/cm<sup>3</sup>.

[Claim 2] The carbon material for electrodes according to claim 1 wherein true density is more than 2.21 g/cm<sup>3</sup>.

[Claim 3] The carbon material for electrodes according to claim 1 or 2 wherein a BET specific surface area is less than 18 m<sup>2</sup>/g.

[Claim 4] The carbon material for electrodes according to any one of claims 1 to 3 wherein

mean particle diameter is 2-50 micrometers.

[Claim 5]The carbon material for electrodes according to any one of claims 1 to 4 wherein the full width at half maximum of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrum is more than  $20\text{ cm}^{-1}$ .

[Claim 6]A multiple layer structure carbon material for electrodes manufactured by carbonizing this organic compound after mixing the carbon material according to any one of claims 1 to 5 with an organic compound.

[Claim 7]In a nonaqueous electrolytic solution secondary battery which has a nonaqueous electrolyte which consists lithium of an anode a cathode and a solute containing occlusion and a carbonaceous material which can be emitted and a nonaqueous solvent A nonaqueous secondary battery wherein said at least some of carbonaceous materials are the carbonaceous materials according to any one of claims 1 to 6.

[Claim 8]Said solute  $\text{LiClO}_4\text{LiPF}_6\text{LiBF}_4\text{LiCF}_3\text{SO}_3\text{LiN}(\text{CF}_3\text{SO}_2)_2$  The nonaqueous secondary battery according to claim 7 which are one or more compounds chosen from  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$  and a group that consists of  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ .

[Claim 9]The nonaqueous secondary battery according to claim 7 or 8 wherein a nonaqueous solvent contains cyclic carbonate and chain carbonate.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the nonaqueous secondary battery which used the carbon material for electrodes and it, the carbon material for electrodes which can constitute the nonaqueous secondary battery which is high capacity and has good quick charge/discharge capability in detail -- it is preferably related with the carbon material for anodes.

[0002]

[Description of the Prior Art]In recent years the rechargeable battery of high capacity is needed with the miniaturization of an electronic device. Especially compared with a nickel-cadmium battery and a nickel hydride battery the lithium secondary battery with a high energy density has attracted attention. Although to use a lithium metal at first was tried as the negative pole material while repeating charge and discharge lithium deposited in the shape of resin (the shape of a dendrite) the separator was penetrated even the cathode reached and it became clear that there was a danger of short-circuiting two poles. Therefore its attention has been paid to the material of a carbon system which can prevent generating of a dendrite instead of a metal electrode.

[0003]The cell which adopted the difficulty black lead nature carbon material with a low degree of crystallinity as the negative pole material as a nonaqueous electrolyte secondary battery which uses a carbon system material was marketed first. Then the cell using black lead with a high degree of crystallinity is marketed and it has continued up to now. The electric capacity of black lead is  $372\text{ mAh/g}$  and the theory top maximum. If an electrolysis solution is chosen appropriately the cell of high charge-and-discharge capacity can be obtained.

Using the carbonaceous material which has multiple layer structure as furthermore shown

in JPH4-171677A is also examined. This combining the strong point (high capacity and irreversible capacity are small) of black lead with high crystallinity demerit (a propylene carbonate system electrolysis solution is disassembled) and the strong point (it excels in stability with an electrolysis solution) and demerit (irreversible capacity is large) of carbonaceous material with a low degree of crystallinity and employing the mutual strong point efficiently. It is based on the idea of compensating demerit.

[0004] Compared with a difficultly black lead nature carbon material crystallinity of black lead (double layer carbonaceous material containing black lead and black lead) is high and its true density is high. Therefore if an anode is constituted using the carbon material of these black lead high electrode restoration nature is obtained and the volume energy density of a cell can be raised. When it constitutes an anode from black lead system powder a binder is mixed with powder the slurry which added carrier fluid is created and this is applied to the metallic foil which is a charge collector.

Then the method of drying carrier fluid is generally used.

Under the present circumstances it is common to establish the process of performing compression molding sticking by pressure to a powdered charge collector and for the purpose of equalization of the polar-plate thickness of an electrode and improvement in polar-plate capacity and also. By this pressing operation the polar-plate density of an anode improves and the energy density per volume of a cell improves further.

[0005] However it is high crystallinity and also industrially the particle shape of an available common graphite material is the shape of a scale lepidic form and tabular. This particle shape is considered to originate in it becoming graphite-crystals nature black lead to be the shape of a scale to be a lepidic form and that it is tabular because a carbon crystal mesh plane carries out lamination growth in one way. When these graphite materials are used for the anode of a nonaqueous electrolyte secondary battery the service capacity with it which has little irreversible capacity is shown because of the crystalline height but.

[big] Since there is little abundance of the crystal edge face which a lithium ion can frequent [particle shape] by the shape of a scale the lepidic form and a tabular thing and there is much abundance of the basal side which does not participate in receipts and payments of a lithium ion the fall of capacity is seen in the rapid charge and discharge in high current density. If graphite particles are polar-plate-ized through the above-mentioned polar-plate manufacturing process polar-plate density will rise according to a degree of compaction but since a particle gap is not fully secured by one side movement of a lithium ion is barred and there is a problem that the quick charge/discharge capability as a cell will fall.

[0006] When tabular graphite particles are fabricated as an electrode the plate surface of a granular material is arranged by an electrode plate side and parallel with high probability under the influence of the application process of a slurry and the pressing operation of a polar plate. Therefore the edge face of the graphite-crystals child who constitutes each granular material particle is comparatively high probability and is fabricated by physical relationship vertical to an electrode surface. When charge and discharge were performed in the state of such a polar plate the lithium ion which moves between positive and negative poles and of which black lead inserts and disconnects itself once needed to turn around the powder surface and also had the problem that it was remarkable and disadvantageous in respect of the move efficiency of the ion in the inside of an electrolysis solution. Since particles were carrying out tabular form the void left behind to

the electrode after shaping also had the problem that it will be shut to the electrode exterior. That is since free circulation of an electrolysis solution with the electrode exterior was barred there was a problem that movement of a lithium ion was barred.

[0007] On the other hand the ratio of the crystal edge face which a lithium ion frequents considers it as the negative pole material which carried out the spherical form which can secure a void required for movement of the lithium ion within a polar plate highly the graphitization thing of meso carbon micro beads is proposed and it is already commercialized. If the form is spherical even if it will pass through an above-mentioned polar-plate pressing operation by the area to which a lithium ion can frequent particles increasing if the ratio of an edge face is high the isotropy of a crack and an edge face is maintained for alternative arrangement by each granular material particle and the movement speed of the ion in the inside of an electrode plate is maintained good. The void which remained inside the electrode originates in the particle shape and since it is in the state connected with the electrode exterior movement of a lithium ion is comparatively free and serves as electrode structure which can respond also to rapid charge and discharge. However since the crystal structure level of meso carbon micro beads as black lead is low the limit of electric capacity is as low as 300 mAh/g and it is already known widely that it is inferior to the shape of a scale and lepidic and tabular black lead.

[0008] Paying attention to these problems invention which specified the form of the black lead used for a nonaqueous electrolyte secondary battery is also performed. JPH8-180873A -- a scale -- invention which specified the ratio etc. of \*\* particles and the particles which are not scales-like comparatively is indicated. one of these -- JPH8-83610A -- this -- reverse -- more -- a scale -- it is indicated that \*\* particles are preferred.

[0009] [Problem to be solved by the invention] The practical use cell is asked for the electrode which combines high electric capacity and the outstanding quick charge/discharge capability. The electrode which fully fills such a demand has not yet come [ however ] to be provided. For this reason to improve the quick charge/discharge capability of the shape of a scale and a lepidic and tabular graphite material especially is desired strongly. Then it made for this invention to solve the problem of conventional technology to meet the demand from such the former into SUBJECT. That is it made to provide the carbon material for electrodes the electrode restoration nature of material is high and is high energy density and which was excellent in quick charge/discharge capability into the issue which should be solved.

[0010] [Means for solving problem] In order to solve above-mentioned SUBJECT as a result of this invention persons' repeating examination wholeheartedly in order to improve the performance of an electrode The thickness direction of the graphite-grains child who maintains high service capacity because the inside of a graphite-grains child is a high crystal and is doing tabular is comparatively thick By what the graphite-grains child who is high [ the rate of an abundance ratio of an edge part ] by what it is [ the thing ] ruined (particles which have a crack and bending in a basal side and the edge part of the crystal exposed to it) is used for. Make the quantity of the portion which a lithium ion can frequent increase and graphite-grains child form more nearly spherically further by raising more nearly isotropic arrangement of particles i.e. isotropic arrangement of an edge part by using a near carbon material with high restoration nature. It came to acquire knowledge

that the electrode which was excellent in high capacity quick charge/discharge capability and a cycle characteristic is obtained.

[0011]The carbon material for electrodes of this invention is completed based on such knowledgeThe spacing (d002) of the field by a wide angle X-ray diffraction method (002) in the first place Less than 0.337 nmThe R value which is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to the peak intensity of  $1580\text{ cm}^{-1}$  [ in / in crystallite size (Lc) / not less than 90 nm and an Ar-ion-laser Raman spectrum ] 0.20 or more. And it is characterized by tap density being more than  $0.75\text{ g/cm}^3$  and this invention[ second ] After mixing with an organic compound the carbon material which has the above-mentioned characteristic as a carbon material for electrodesIt is a thing using the multiple layer structure carbon material obtained by carbonizing this organic compoundIn the nonaqueous electrolytic solution secondary battery which has [ third ] a nonaqueous electrolyte which consists lithium of the anodecathode and solute containing occlusion and the carbonaceous material which can be emittedand an organic system solventSaid at least some of carbonaceous materials are the nonaqueous secondary batteries being a carbonaceous material which has the above-mentioned characteristicor a multiple layer structure carbonaceous material.

[0012]

[Mode for carrying out the invention]Belowthe carbon material for electrodesthe multiple layer structure carbon material for electrodesand rechargeable battery of this invention are explained in detail.

[0013]A spacing (d002) and crystallite size (Lc) of a field according [ a carbon material for electrodes of carbon material this invention for electrodes ] to a wide angle X-ray diffraction method (002)And an R value which is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to peak intensity of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrumand tap density are characterized by being in a predetermined range. That is a spacing (d002) of a field according [ a carbon material for electrodes of this invention ] to a wide angle X-ray diffraction method (002) is less than 0.337 nm and crystallite size (Lc) is not less than 90 nm. An R value which is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to peak intensity of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrum a carbon material for electrodes of this invention 0.20 or more. 0.25 or more things can be chosen and used especially especially preferably 0.23 or more preferably. The maximum of an R value should just be 0.9 or less and 0.5 or less are [ 0.7 or less ] especially preferably preferred. A carbon material for electrodes of this invention is characterized by tap density being more than  $0.75\text{ g/cm}^3$  and it is more than  $0.80\text{ g/cm}^3$  preferably and as for a maximum below  $1.40\text{ g/cm}^3$  is  $1.20\text{ g/cm}^3$  more preferably.

[0014]A spacing (d002) and crystallite size (Lc) of a field by a wide angle X-ray diffraction method (002) show that it is a value showing the crystallinity of carbon material bulk and it is a high crystalline carbon material also that crystallite size (Lc) is so large that a value of a spacing (d002) of a field (002) is small. An R value which is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to peak intensity of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrum in this invention is an index showing crystallinity near the surface of a carbon particle (about [ from a particle surface ] 100Å)Crystallinity is so low that an R value is larger it is shown that a crystallized state is confused.

[0015]In this invention a spacing (d002) of a field by a wide angle X-ray diffraction method (002) Namely less than 0.337 nm Although the crystallinity of a carbon particle is

high carbon material for electrodes whose R value which crystallite size ( $L_c$ ) is not less than 90 nm and is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to peak intensity of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrum is 0.20 or more. It is shown that it is ruined and abundance of a state with much distortion, i.e., an edge part is high. A carbon material for electrodes whose tap density is more than  $0.75\text{ g/cm}^3$  shows that a filling factor of an electrode is high and particle shape has a radius of circle.

[0016] "Tap density" as used herein means bulk density after carrying out 1000 times tapping and it is expressed with the following formulas.

[Mathematical formula 1] Tap density = a filling body product of the mass/granular material of a restoration granular material [0017] Although packing structure of granular material particles is influenced by grade of a size of particles and interparticle interaction power etc., on these Description tap density is being used for it as an index which argues about packing structure quantitatively. Various formulas are proposed as a formula showing a tap restoration action. As the example it is a following formula. :

[Mathematical formula 2]  $\rho_n = A \cdot \exp(-k \cdot n)$

\*\*\*\*\* -- things are made. Bulk density [in  $\rho$  / an end of restoration] and  $\rho_n$  are [here] the bulk density at the time of  $n$  times restoration and  $k$  and  $A$  are constants. "Tap density" as used in this Description considers that bulk density at the time of 1000 times-tapping restoration to a  $20\text{ cm}^3$  cell ( $\rho_{1000}$ ) is final bulk density  $\rho$ .

[0018] As long as a carbon material for electrodes of this invention fulfills these conditions, other physical properties in particular are not restricted. However, the desirable range of other physical properties is as follows. Within the limits whose mean particle diameter is 2-50 micrometers is preferred for a carbon material for electrodes of this invention, it is preferred that it is within the limits which is 4-35 micrometers, it is more preferred that it is within the limits which is 5-27 micrometers, and it is still more preferred that it is a range which is 7-19 micrometers. A range indicated by "-" in this Description shows a range including a numerical value indicated before and behind "-."

[0019] As for especially the carbon material for electrodes of this invention, it is preferred that a BET specific surface area is below  $13\text{ m}^2/\text{g}$  in less than  $18\text{ m}^2/\text{g}$  and also below  $15\text{ m}^2/\text{g}$ . It is preferred that the full width at half maximum of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrum is more than  $20\text{ cm}^{-1}$  as for a maximum, it is preferred that it is below  $27\text{ cm}^{-1}$  and especially  $21\text{--}26\text{ cm}^{-1}$  can be chosen and used. As for the carbon material for electrodes of this invention, it is preferred that true density is more than  $2.21\text{ g/cm}^3$ ; it is more preferred that it is more than  $2.22\text{ g/cm}^3$  and it is especially preferred that it is more than  $2.24\text{ g/cm}^3$ .

[0020] In the flow type particle image analysis meter which the carbon material for electrodes of this invention photos at a time thousands of one particle distributed in liquid using a CCD camera and can compute the average shape parameter, that from which the degree of mean circle form for all the particles (the boundary length of a granular structure product equivalent circle is used as a numerator, it is set to 1 by the ratio which made the denominator the boundary length of the picturized particle projection image so that a particle image is close to a perfect circle and a particle image is long and slender or it becomes such a small value that convex or concave is carried out) becomes 0.940 or more is preferred. The carbon material for electrodes of this invention, the G value which is the surface ratio of the peak area (integral value of  $1480\text{--}1680\text{ cm}^{-1}$ ) near  $1580\text{ cm}^{-1}$  to the peak area near  $1360\text{ cm}^{-1}$  in an argon laser Raman spectrum (integral value of  $1260\text{--}$

1460 cm<sup>-1</sup>) It is less than 2.5 more preferably and although there is no restriction in particularity is [ less than 3.0 ] preferably preferred [ a minimum ] that it is 1.0 or more. [0021] Even if it uses a carbon material produced naturally a carbon material manufactured artificially may be used for a carbon material for electrodes of this invention. A manufacturing method in particular of a carbon material for electrodes of this invention is not restricted either. Therefore a carbon material for electrodes which has the above-mentioned characteristic for example using judgment means such as sieving and pneumatic elutriation can also be sorted out and acquired. The most desirable manufacturing method is a method of adding and reforming dynamic energy processing to a carbon material produced naturally or a carbon material manufactured artificially and manufacturing a carbon material for electrodes. Then this mechanical energy processing is explained below.

[0022] Carbon materials of a raw material used as an object which adds mechanical energy processing are natural or artificial graphite powder and carbonaceous powder which is black lead precursors. Such graphite powder and carbonaceous powder have that preferred whose true density less than 0.340 nm and crystallite size (Lc) are not less than 30 nm and a spacing (d002) is more than 2.25 g/cm<sup>3</sup>. That whose spacing (d002) is less than 0.338 nm especially is more preferred and what is less than 0.337 nm is still more preferred. As for crystallite size (Lc) what is not less than 90 nm is more preferred and what is not less than 100 nm is still more preferred. As for mean particle diameter what is not less than 10 micrometers is preferred what is not less than 15 micrometers is more preferred what is not less than 20 micrometers is still more preferred and what is not less than 25 micrometers is further more preferred. About a maximum of mean particle diameter what is 1 mm or less is preferred what is 500 micrometers or less is more preferred what is 250 micrometers or less is still more preferred and what is 200 micrometers or less is further more preferred.

[0023] Graphite powder and carbonaceous powder can be used as a raw material even if crystallinity is high and it is low. Since a raw material with low crystallinity has comparatively low plane orientation nature and structure has disorder a crushing surface is comparatively isotropic and it is easy to obtain roundish treating material by performing mechanical energy processing. After performing mechanical energy processing crystallinity can be improved if it heat-treats further.

[0024] In a carbon material used as an object which adds mechanical energy processing black lead for your kind consideration into which a hex-steel side was greatly grown up in plane orientation and isotropic high-density black lead which gathered isotropically a graphite-grains child-oriented [ of your kind consideration ] can be mentioned as a high crystallinity carbon material in which a carbon hex-steel plane structure progressed. As black lead for your kind consideration natural graphite from Sri Lanka or a MADAKA scull and an artificial graphite of a high degree of graphitization of what is called kish graphite and a part deposited as carbon of supersaturation from iron which carried out melting can be illustrated as a suitable thing.

[0025] Natural graphite according to the description Scaly graphite (Flake Graphite) Flaky graphite (Crystalline (Vein) Graphite) it is classified into soil black lead (Amorphous Graphite) ("particulate matter process technology collection" (Industrial technique Center.)) Refer to a clause of black lead of the Showa 49(1974) issue and "HANDBOOK OF CARBON GRAPHITE DIAMOND AND FULLERENES" (Noyes Publications issue).

Although flaky graphite of a degree of graphitization is the most expensive at 100% and scaly graphite is expensive at 99.9% after this soil black lead is as low as 28%. Scaly graphite which is natural graphite is produced to Madagascar China Brazil the Ukraine Canada etc. and flaky graphite is mainly produced to Sri Lanka. Soil black lead makes the Korean Peninsula China Mexico etc. the main origins. In these natural graphite generally particle diameter is small and also soil black lead has low purity. On the other hand since there are the strong points like a degree of graphitization and impurity quantity are low scaly graphite and flaky graphite can be preferably used in this invention. [0026] An artificial graphite can be manufactured by heating petroleum coke or coal pitch coke at 1500-3000 °C or the temperature beyond it under a non-oxidizing atmosphere. In this invention if for your kind consideration and high Electrochemistry Sub-Division capacity are shown after performing mechanical energy processing and heat treatment any artificial graphite can be used as a raw material.

[0027] Mechanical energy processing to these carbon materials is performed so that the mean-particle-diameter ratio before and behind processing may become one or less. "The mean-particle-diameter ratio before and behind processing" is the value which  $\frac{\text{mean particle diameter before processing}}{\text{mean particle diameter after processing}}$  with the mean particle diameter before processing the mean particle diameter after processing. Mean particle diameter here is the particle size distribution of the volume reference measured with laser type particle-size-distribution measuring apparatus. If it measures with laser type particle-size-distribution measuring apparatus the particle size distribution which also equalized the particles which have anisotropy in form isotropic and converted them as a ball substantially will be acquired.

[0028] It is made for the mean-particle-diameter ratio before and behind processing to become one or less in the mechanical energy processing which manufactures the carbon material for electrodes of this invention and which is performed for accumulating. On the other hand if granulation is carried out a mean-particle-diameter ratio will be one or more and tap density will also rise. Since returning to the state before processing in the process fabricated eventually is fully expected the particulate matter which carried out granulation is not preferred.

[0029] Mechanical energy processing controls particle shape at the same time it reduces grain size so that the mean-particle-diameter ratio before and behind processing of a powder particle may become one or less. In engineering unit operation utilizable for the particle design of grinding classification mixing granulations surface treatment reaction etc. mechanical energy processing belongs to grinding treatment.

[0030] Grinding applies power to a substance decreases the size and refers to adjusting the particle diameter of a substance particle size distribution and restoration nature. Grinding treatment is classified according to the kind of power applied to a substance and processing. The power applied to a substance is divided roughly into four the power (impulse force) struck and broken the power (compressive force) to crush the power (grinding power) to mash and the power (shearing force) to shave off. On the other hand processing is divided roughly into two the bulk crushing which is made to generate a crack inside particles and is made to spread and the surface grinding cutting off a particle surface. Bulk crushing advances according to impulse force compressive force and shearing force and surface grinding advances according to grinding power and shearing force. Grinding is the processing which combined variously the kind and processing of the power applied to these substances. The combination can be suitably determined



according to a processing purpose.

[0031] Although grinding may be performed using chemical reactions and cubical expansions such as blasting, it is common to carry out using mechanical apparatus such as a grinder. As for the grinding treatment used for manufacture of the carbon material for electrodes of this invention, it is preferred that it is processing in which the rate that is not concerned with the existence of bulk crushing but a surface treatment occupies eventually becomes high. That is because the surface grinding of particles takes the angle of graphite particles or a carbonaceous particle and introduces a radius of circle into particle shapes so it is important. After bulk crushing progresses to some extent, a surface treatment may specifically be performed only a surface treatment may be performed for bulk crushing to \*\*\*\*\* and bulk crushing and a surface treatment may be performed further simultaneously. It is preferred to perform grinding treatment which surface grinding progresses eventually and is polished from the surface of particles.

[0032] The equipment which performs mechanical energy processing is chosen from what has possible performing the above-mentioned desirable processing. When this invention persons inquired, it became clear that the equipment which repeats mechanical works which also included the interaction of particles for impulse force in the subjects such as compression, friction and shearing force and is given to particles is effective. When it has the rotor which installed many blades and the rotor specifically carries out a high velocity revolution to the inside of a casing, the equipment which performs a surface treatment is preferred giving mechanical works such as shock compression, friction and shearing force to the carbon material introduced into the inside and advancing bulk crushing. It is more preferred by circulating or circulating a carbon material that it is what has a mechanism in which a mechanical work is repeated and given.

[0033] Nara Machine Factory hybridization system can be mentioned as an example of such desirable equipment. When processing using this equipment, it is preferred to carry out [ second ] peripheral velocity of the rotor to rotate in 30-100 m / it is more preferred to carry out [ second ] in 40-100 m / and it is still more preferred to carry out [ second ] in 50-100 m /. Although it is also possible to pass a carbon material as for processing, it is preferred to make the inside of 30-second or more equipment circulate or stagnate and to process it and it is more preferred to make the inside of 1-minute or more equipment circulate or stagnate and to process it.

[0034] It is preferred that it performs heat treatment which improves crystallinity further after performing mechanical energy processing when true density of carbonaceous powder used as a raw material is not [ crystallinity ] so high at less than 2.25. It is preferred to perform heat treatment above 2000 °C; it is more preferred to carry out above 2500 °C; and it is still more preferred to carry out above 2800 °C. While graphite particles or a carbonaceous particle had maintained high crystallinity on the whole by performing such mechanical energy processing, only the neighborhood of the surface of particles becomes coarse and serves as particles which distortion and an edge face exposed. By this field which a lithium ion can frequent will increase and it will have high capacity also in high current density.

[0035] As an index of the crystallinity of particles and granularity of a particle surface, the edge face abundance of a crystal, an R value which is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to peak intensity of  $1580\text{ cm}^{-1}$  in a spacing ( $d_{002}$ ), crystallite size (Lc) and an Ar-ion-laser Raman spectrum of a field by a wide angle X-ray diffraction method (002)

can be used. Generally value of a carbon material of a spacing ( $d_{002}$ ) of a field ( $002$ ) is small and crystallite size ( $L_c$ ) of an R value is as small as a large thing. That is graphite particles or the whole carbonaceous particle is the almost same crystallized state. On the other hand although a carbon material for electrodes of this invention has a small value of a spacing ( $d_{002}$ ) of a field ( $002$ ) and crystallite size ( $L_c$ ) is large an R value has taken a large value. That is although the crystallinity of carbon material bulk is high crystallinity near the surface of a carbon particle (about [ from a particle surface ] 100Å) is confused and it means that exposure of an edge face has increased. This mechanical energy processing can introduce a radius of circle into particles and can raise the restoration nature of these particles.

[0036] In order to improve the restoration nature of granular material particles it is known that it is good to be filled up with the smaller particles which can enter the void made between particles. For this reason if grinding etc. are processed and particle diameter is made small to carbonaceous or graphite particles it is possible that restoration nature increases but even if it makes particle diameter small by such a method generally restoration nature will fall on the contrary. It is thought that it is because particle shape becomes an infinite form more by grinding as this cause.

[0037] On the other hand the rate that the void of a packed bed occupies falls so that there is much number (coordination number  $n$ ) of particles in contact with the one particles (view particles) in a granular material particle group. That is a factor which affects a filling factor the size ratio of particles and composition ratio i.e. particle size distribution are important. However the carbonaceous or the graphite particles before the processing which this examination is performed by the spherical particle group like a model and is dealt with by this invention Even if particle size distribution is controlled by the shape of a scale lepidic form tabular and only general grinding a classification etc. and it tries a filling factor with the method of being higher so much high filling state cannot be produced.

[0038] Generally the shape of a scale lepidic and tabular carbonaceous or graphite particles are in the tendency for restoration nature to get worse so that particle diameter becomes small. Particles infinite-form-ize this more by grinding and on the surface of particles "Peel and write" [ a "split" and ] It thinks for protuberance form things such as "bending" to carry out the increase in generation and also for resistance between contiguity particles to become large and to worsen restoration nature by the cause of adhering to more detailed indeterminate form particles by a certain amount of intensity in a particle surface. These infinite form nature should decrease if particle shape approaches a globular form even if particle diameter will become small reduction of restoration nature should decrease and tap density comparable also at large diameter carbon powder or the diameter carbon content of a granule will be shown theoretically.

[0039] By this invention persons' examination by carbonaceous or graphite particles also with almost equal true density and almost equal mean particle diameter it is checked that a value with high tap density is shown so that form is spherical. That is it is important to make form of particles roundish and to bring close to it spherically. If particle shape approaches spherically restoration nature's of a granular material will improve greatly simultaneously. In this invention tap density of a granular material is adopted as an index of the degree of conglomeration for the above Reason. When the restoration nature of a particulate matter after processing is going up compared with processing before a result in

which particles spheroidized can be considered with a used disposal method. A result of having spheroidized can be considered if tap density of a carbon material obtained when it processes reducing particle diameter greatly in a method of this invention is a high value compared with tap density of a carbon material of comparable particle diameter obtained by general grinding.

[0040] In this invention after performing mechanical energy processing carbonaceous or graphite particles which performed a classification and removed fines and/or a rough part can also be used. A publicly known technique can be used for a classification. An R value which is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to peak intensity of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrum by performing above-mentioned processing by 0.01-0.25. Raw material graphite powder whose crystallite size (Lc) a spacing (d002) of a field by a wide angle X-ray diffraction method (002) is less than  $0.337\text{ nm}$  and is not less than  $90\text{ nm}$  by performing mechanical energy processing 1.5 or more times of an R value of graphite powder before an R value which is a peak intensity ratio of  $1360\text{ cm}^{-1}$  to peak intensity of  $1580\text{ cm}^{-1}$  in an Ar-ion-laser Raman spectrum processing. Although more than twice and a maximum in particular are not limited preferably usually Ten or less times Seven or less times can be adopted preferably and a carbon material for electrodes whose crystallite size (Lc) a spacing (d002) of a field by a wide angle X-ray diffraction method (002) is less than  $0.337\text{ nm}$  and is not less than  $90\text{ nm}$  and whose tap density is the graphite powder by which it was processed more than  $0.75\text{ g/cm}^3$  can be provided.

[0041] The multiple layer structure carbon material for electrodes of multiple layer structure carbon material this invention for electrodes can be prepared by baked-carbonizing this organic compound after mixing the organic compound carbonized by the baking process and the carbon material for electrodes of this invention which has said characteristic. If the organic compound mixed with the carbon material for electrodes is carbonized by calcinating the kind in particular will not be restricted. Therefore even if it is an organic compound which advances carbonization by the liquid phase it may be an organic compound which advances carbonization by the solid phase. The organic compound mixed with the carbon material for electrodes may be a single organic compound or may be a mixture of two or more sorts of organic compounds.

[0042] As an organic compound to advance carbonization by the liquid phase The coal tar pitch from a soft pitch to a hard pitch Direct-current system heavy oils such as Carboniferous system heavy oils such as coal liquid and asphaltene crude oil Heat treatment pitch such as an ethylene tar pitch FCC decantation oil the Ashland pitch etc. which are obtained by heat-treating petroleum system heavy oils such as naphtha tar division-into-equal-parts solution system heavy oil which carries out a byproduct at the time of pyrolysis such as naphtha and decomposition system heavy oil etc. can be used. Furthermore polyvinyl chloride polyvinyl acetate polyvinyl butyral A vinyl system polymer and 3-methyl phenol formaldehyde resin such as polyvinyl alcohol Substances such as sulfur ring compound such as nitrogen ring compound such as aromatic hydrocarbons such as substitution phenol resin such as 35-dimethylphenol formaldehyde resin an acenaphthylene decacyclene and anthracene phenazine and an acridine and a thiophene can be raised.

[0043] As an organic compound which advances carbonization by the solid phase Chain polyvinyl resin such as naturally-occurring polymers such as cellulose polyvinylidene chloride and polyacrylonitrile Thermosetting resin such as aromatic system polymers such as

polyphenylene furfuryl alcohol resin phenol-formaldehyde resin and imide resin a thermosetting resin raw material like furfuryl alcohol etc. can be mentioned. They can be used by choosing a solvent suitably and carrying out dissolution dilution if needed making these organic compounds adhere on the surface of a powder particle. The typical manufacturing method which consists of the following processes as a method of manufacturing the multiple layer structure carbon material for electrodes of this invention from these organic compounds and the carbon material for electrodes can be illustrated. [0044] (The 1st process) The process of mixing an organic compound with the carbon material for electrodes using a mixer a kneading machine etc. of various marketing if needed with a solvent and obtaining a mixture.

(The 2nd process) (process carried out if needed)

The process of obtaining the intermediate product which heated having remained as it is or agitating as occasion demands and removed the solvent for said mixture.

(The 3rd process) The process of heating said mixture or an intermediate product at 500-3000 °C under inert gas atmosphere such as nitrogen gas carbon dioxide and argon gas or a non-oxidizing atmosphere and obtaining the quality of carbonized material.

(The 4th process) (process carried out if needed)

A process of carrying out [ classifying processing / grinding cracking ] granular material processing of said quality of carbonized material.

[0045] When mixing the first process a solvent may be used and it is not necessary to use it. When using a solvent in particular the kind and quantity are not restricted but a solvent which dissolves the above-mentioned organic compound which uses it or falls viscosity is preferred. Although temperature in particular at the time of mixing is not restricted either a room temperature to 100 °C or less 200 °C or less of 300 °C or less is more preferably used by room temperature from a room temperature for example. An organic compound can be made to adhere to the surface of a powder particle of a carbon material for electrodes by mixing a carbon material for electrodes with an organic compound in the first process. Not less than 400 °C of cooking temperature of the 2nd process is not less than 300 °C usually not less than 500 °C still more preferably preferably and although a maximum in particular is not limited it is 1500 °C or less especially preferably 2500 °C or less still more preferably 2800 °C or less preferably 3000 °C or less. Although the 2nd process can also be omitted the 3rd process is performed after usually performing the 2nd process and obtaining an intermediate product.

[0046] In heat-treatment of the 3rd process heat history temperature conditions are important. Although the lower limit temperature changes a little with kinds and heat histories of an organic compound usual [ not less than 500 °C of / not less than 700 °C of ] is not less than 900 °C still more preferably preferably. 3000 °C or less of upper limit temperature [ 2800 °C or less of / 2500 °C or less of ] is usually 1500 °C or less especially preferably still more preferably preferably. A heating rate a cooling rate a heat treating time etc. can be arbitrarily set up according to the purpose. After heat-treating comparatively in a low temperature region temperature up can also be carried out to a predetermined temperature. Omitting is also possible although the 4th process is a process of performing grinding cracking division processing etc. and carrying out granular material processing if needed. The 4th process can also be performed before the 3rd process and can also be performed in great numbers before and after the 3rd process. A batch process or continuous system may be sufficient as a reaction machine used for

these processes. Kazumoto or two or more sets may be sufficient.

[0047]The carbonaceous material of the organic compound origin in the multiple layer structure carbon material for electrodes of this invention is comparatively (henceforth "coverage") usually preferred 0.1 to 50weight %and 0.5 to 25weight %more preferably adjusts one to 15weight % so that it may become 2 to 10 weight % still more preferably. Volume reference mean particle diameter is preferred 2-70 micrometersand 4-40 micrometers of multiple layer structure carbon materials [ 5-35 micrometers of ] for electrodes of this invention are 7-30 micrometers still more preferably more preferably. the specific surface area measured using the BET adsorption method -- for example0.1-10m<sup>2</sup>/g -- desirable -- 1-10m<sup>2</sup>/g -- further -- desirable -- 1-7m<sup>2</sup>/g -- it is 1-4m<sup>2</sup>/g especially preferably. As for the multiple layer structure carbon material for electrodes of this inventionin the diffraction diagram of the X ray wide angle diffraction which made CuK alpha rays the line sourceit is preferred not to exceed the degree of crystallinity of the carbonaceous used as a core or graphite particles.

[0048]In the Raman-spectrum analysis for which the multiple layer structure carbon material for electrodes of this invention used the Ar-ion-laser light of wavelength [ of 5145 cm<sup>-1</sup> ]The R value expressed with the ratio "IB/IA" of the peak PB (peak intensity IB) which appears in the range of 1350-1370 cm<sup>-1</sup> to peak PA (peak intensity IA) which appears in the range of 1580-1620 cm<sup>-1</sup> desirable -- 0.1 to 0.7 -- further -- desirable -- 0.20 to 0.7 -- it is 0.25-0.6 especially preferably. tap density -- 0.70-1.40g/cm<sup>3</sup> -- it is preferably desirable 0.75-1.40g/cm<sup>3</sup> and to control in the range of 0.85 - 1.40 g/cm<sup>3</sup> still more preferably. By multiple layer structure-izationsince the tap density of the carbon material for electrodes improves furtherthe effect that the form introduces a radius of circle further may show up. The particle surface of the carbon material of this invention for electrodes is ruinedand when it uses for the multiple layer structure carbon material for electrodes of this inventionthe effect that a binding property with the covered carbonaceous material increases can also be expected.

[0049]An electrode can be manufactured using a carbon material for electrodes of electrode this inventionor a multiple layer structure carbon material for electrodes. Especially a multiple layer structure carbon material for electrodes of this invention can be used for manufacture of an electrode very preferably. The manufacturing method in particular is not restrictedbut can be manufactured in accordance with a method generally used. A method of applying a slurry obtained by adding a binding agenta solventetc. to a carbon material for electrodes or a multiple layer structure carbon material for electrodesand making it slurry form as a typical method to a substrate of metal charge collectorssuch as copper foiland drying can be mentioned. Pack density of a polar plate can be raised and the amount of electrodes per unit volume can be made to increase by carrying out the consolidation of what carried out spreading desiccation of a carbon material for electrodesor the multiple layer structure carbon material for electrodes with a roll pressa compression molding machineetc. Furthermore a carbon material for electrodes or a multiple layer structure carbon material for electrodes can also be fabricated by methodssuch as compression moldingin form of an electrode.

[0050]As a binding agent which can be used for electrode manufactureTo a solventstable polyethylene and polypropylenepolyethylene terephthalateResin system polymerssuch as aromatic polyamide and cellulosestyrene-butadiene rubberRubber-like polymerssuch as polyisoprene rubberbutadiene rubberand ethylenec-propylene rubberStyrene butadiene

styrene block copolymer styrene isoprene styrene block copolymer Thermoplastic-elastomer-like polymers such as the hydrogenation thingsyndiotactic 1,2-polybutadieneElasticity resin-like polymers such as an ethylene-vinyl acetate copolymerpropylene alpha olefin (carbon numbers 2-12) copolymerFluorine system polymers such as polyvinylidene fluoride vinylidene fluoride hexachloropropylene copolymerpolytetrafluoroethyleneand a polytetrafluoroethylene ethylenic copolymerare mentionedand Polymer Compounds Sub-Division which has the ion conductivity of a lithium ion further is also mentioned. [0051]As a polymer which it has ion conductivity Polyether system high molecular compoundssuch as polyethylene oxide and polypropylene oxideThe bridging body polymer of a polyether compoundpolyepichlorohydrinpolyphosphazeneA polysiloxane polyvinyl pyrrolidonepolyvinylidene carbonateThe system which compounded lithium salt or the alkaline metal salt which makes lithium a subject with high molecular compoundssuch as polyacrylonitrileOr the system which blended with this the organic compound which has high dielectric constantssuch as propylene carbonateethylene carbonateand gamma-butyrolactoneand the organic compound of hypoviscositysuch as straight-chain-shape carbonatecan be used. The ionic conductivity in such a room temperature of ion-conductive Polymer Compounds Sub-Division of more than  $10^{-5}$  s/cm is more than  $10^{-3}$  s/cm more preferably.

[0052]Various kinds of forms can be taken as mixed form of the carbon material for electrodes or the multiple layer structure carbon material for electrodesand a binding agent. For examplethe form which both particles mixedthe form mixed in the form where a fibrous binding agent becomes entangled with the particles of carbonaceous material the form with which the layer of the binding agent adhered to the particle surface of carbonaceous material can be mentioned. As for both mixing ratioit is preferred to carry out a binding material to 0.1 to 30weight % to the carbon material for electrodes or the multiple layer structure carbon material for electrodesand it is more preferred to carry out to 0.5 to 10weight %. If 30weight % or more of a binding material is addedthe internal resistance of an electrode will become largeand at 0.1 or less weight %it is in the tendency which is inferior in the binding property of a charge collectorthe carbon material for electrodesor the multiple layer structure carbon material for electrodes conversely.

[0053]The electrode which consists of a carbon material for electrodes of this inventionor a multiple layer structure carbon material for electrodesThe density (it is called electrode density below) of the active material layer on the electrode by which consolidation was carried out by performing a roll presscompression moldingetc.  $0.5-1.7\text{ g/cm}^3$ The maximum size can pull out the capacity per unit volume of a cellwithout spooling efficient discharge and the low-temperature characteristic preferably  $0.7-1.6\text{ g/cm}^3$  and by considering it as  $0.7-1.55\text{ g/cm}^3$  still more preferably. At this timethe carbon material for electrodes of this inventionor the multiple layer structure carbon material carbon material for electrodes. The edge part is exposed from the surface of the statei.e.particleswhose surface of particles was high because the crystallinity inside particles is highand was ruined. [ of charge-and-discharge capacity ] Because or it is the particle shape (particle shape where whose rate of the edge part was pulverized by the field and rectangular directions of tabular particlesand the thickness direction in particles became relatively thicknamelyincreased) whose abundance of an edge part increases. The dope or the area

dedoped of a lithium ion to the carbon material for electrodes or the multiple layer structure carbon material carbon material particles for electrodes increases. It is possible that diffusion of a lithium ion is more smoothly performed rare [ it / to shut the void in an electrode ] therefore because tap density is high. e.a carbon material is close to a globular form.

[0054]The carbon material for electrodes of rechargeable battery this invention and the multiple layer structure carbon material for electrodes are useful as an electrode of a cell. It is very useful as a negative pole material of nonaqueous secondary batteries such as a lithium secondary battery especially. For example the nonaqueous secondary battery which constituted the metal chalcogenide type cathode and carbonate system solvent for lithium ion batteries by which normal use is carried out to the anode produced in accordance with the above-mentioned method combining the organic electrolysis liquid made into a subject Capacity is large the irreversible capacity accepted in an initial cycle is small rapid charge-and-discharge capacity is high and a cycle characteristic is excellent the preservability and reliability of a cell in the neglect under an elevated temperature are high and it excels in an efficient discharge characteristic and the discharge characteristic in low temperature extremely. In particular about selection of a required component it is not restricted on battery constructions such as a cathode an electrolysis solution etc. which constitute such a nonaqueous secondary battery. Although the material etc. of the component which constitutes a nonaqueous secondary battery below are illustrated the material which can be used is not limited to these examples.

[0055]In the cathode which constitutes the nonaqueous secondary battery of this invention. For example transition metal oxide materials such as lithium transition metal multiple oxide material; manganese dioxides such as a lithium cobalt oxide a lithium nickel oxide and a lithium manganic acid ghost; the material occlusion and can emit lithium such as carbonaceous materials such as graphite fluoride can be used. Specifically  $\text{LiFeO}_2$ ,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and these non-stoichiometric compounds  $\text{MnO}_2$ ,  $\text{TiS}_2$ ,  $\text{FeS}_2$ ,  $\text{Nb}_3\text{S}_4$ ,  $\text{Mo}_3\text{S}_4$ ,  $\text{CoS}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ ,  $\text{CrO}_3$ ,  $\text{V}_3\text{O}_3$ ,  $\text{TeO}_2$ ,  $\text{GeO}_2$  etc. can be used. The manufacturing method in particular of a cathode is not restricted but can be manufactured by the manufacturing method of the above-mentioned electrode and the same method.

[0056]It is preferred to use the valve metal which forms a passive film in the surface by anodization in an electrolysis solution or its alloy for the positive pole collector used by this invention. As a valve metal the metal belonging to IIIa, Va and Va fellows (3B, 4B, 5B fellows) and these alloys can be illustrated. The alloy containing aluminum, Ti, Zr, Hf, Nb, Ta and these metal can specifically be illustrated and the alloy containing aluminum, Ti, Ta and these metal can be used preferably. Since especially aluminum and its alloy are lightweight their energy density is high and is desirable.

[0057]As an electrolysis solution used for the nonaqueous secondary battery of this invention what dissolved the solute (electrolyte) in the nonaqueous solvent can be used. As a solute alkaline metal salt, quaternary ammonium salt, etc. can be used. Specifically  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_2$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  It is preferred to use one or more compounds chosen from  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$  and the group that consists of  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ .

[0058]As a nonaqueous solvent ethylene carbonate, propylene carbonate, cyclic carbonates such as butylene carbonate and vinylene carbonate, chain ethers such as cyclic

ester compound; such as gamma-butyrolactone and 2-dimethoxyethane; Crown ether cyclic ethers such as 2-methyltetrahydrofuran, 12-dimethyltetrahydrofuran, 13-dioxolane and a tetrahydrofuran; chain carbonates such as diethyl carbonate, ethyl methyl carbonate and dimethyl carbonate etc. can be used. A solute and a solvent may choose and use one kind respectively and may mix and use two or more sorts. That in which a nonaqueous solvent contains cyclic carbonate and chain carbonate is preferred also in these.

[0059] In particular construction material or form of a separator that are used for a nonaqueous secondary battery of this invention are not restricted. It dissociates so that a cathode and an anode may not contact physically and ionic permeability of a separator is high and it is preferred that electrical resistance is low. A separator is stable to an electrolysis solution and it is preferred to choose from materials excellent in solution retention. The above-mentioned electrolysis solution can be made to specifically impregnate using a porous sheet or a nonwoven fabric which uses polyolefin such as polyethylene and polypropylene as a raw material.

[0060] Especially the method of manufacturing the nonaqueous electrolytic solution secondary battery of this invention which has a nonaqueous electrolyte anode and a cathode at least can be suitably chosen from the methods which are not limited but are usually adopted. An outer can separator gasket an obturation board a cell case etc. other than a nonaqueous electrolyte anode and a cathode can also be used for the nonaqueous electrolytic solution secondary battery of this invention if needed. The process puts an anode for example on an outer can it can form an electrolysis solution and a separator on it it can put a cathode so that it may counter with an anode further and it can use it as a cell in total in a gasket and an obturation board. The form in particular of a cell is not restricted but can be made the coin type etc. which laminated the cylinder type pellet electrode and separator of the inside-out configuration which combined the cylinder type pellet electrode and separator which made the sheet electrode and the separator spiral shape.

[0061]

[Working example] An example is given to below and this invention is explained to it still more concretely. Material the amount used a rate operation etc. which are shown in the following examples can be suitably changed unless it deviates from the meaning of this invention. Therefore the range of this invention is not restricted to the example shown below.

[0062] (Embodiment 1) 18 kinds of carbon materials for electrodes were prepared by processing a graphite material of the specified quantity indicated in Table 1 by a processing condition indicated in Table 1. A kind of graphite material used as a raw material is as being indicated in Table 3. A result measured with a measuring method which mentions the physical properties of 18 kinds of prepared carbon materials for electrodes later is shown in Table 1.

[0063]

[Table 1]

[0064] (Embodiment 2) It mulled by feeding into M20 type rhe DIGE mixer by Pine Bow company (content volume of 20 l.) 3 kg of carbon materials and 1 kg of petroleum system



tar which are indicated in Table 2. Then after carrying out temperature up and carrying out detarring processing to 700 °C under a nitrogen atmosphere it heat-treated by carrying out temperature up to 1300 °C. Obtained thermally treated material was cracked in a pin mill classifying processing was performed in order to remove a coarse particle and 13 kinds of multiple layer structure carbon materials for electrodes were prepared eventually. A result measured with a measuring method which mentions the physical properties of 13 kinds of prepared multiple layer structure carbon materials for electrodes later is shown in Table 2.

[0065]

[Table 2]

[0066] The details of the graphite material used in Embodiments 1 and 2 are shown in the following table 3.

[0067]

[Table 3]

[0068] The property measuring method of the carbon material prepared in Embodiments 1 and 2 is shown below.

(1) Add about 15% of X ray standard high-purity-silicon powder to the carbon material for X diffraction electrodes and it mixes. The obtained mixture was filled in the sample cell and by making into a line source the CuK alpha rays monochromatized by the graphite monochromator by the reflection type diffractometer method the wide angle X diffraction curve was measured and it asked for a spacing ( $d_{002}$ ) and crystallite size ( $L_c$ ) using Gakushin method.

(2) Raman-spectrum analysis was conducted using NR-1800 by the Raman assay date duty light company. Laser power was set as 30 mW and analysis was conducted by setting exposure time as 75 seconds using Ar-ion-laser light with a wavelength of 514.5 nm. In 30 mW and a test portion part laser power was 18 mW in the light source part by the laser beam attenuation by the optical path between light source sample sections. Sample restoration to a measuring cell was performed by carrying out the natural fall of the carbon material for electrodes and measurement was performed rotating a cell in a field vertical to a laser beam irradiating the sample surface in a cell with a laser beam. The intensity IA of peak PA near  $1580\text{ cm}^{-1}$  of the obtained Raman spectrum and the intensity IB of the peak PB near  $1360\text{ cm}^{-1}$  were measured and the full width at half maximum near the intensity ratio ( $R=IB/IA$ ) and  $1580\text{ cm}^{-1}$  was measured. Area (integral value of  $1260\text{--}1460\text{ cm}^{-1}$ ) of the peak PB near YA and  $1360\text{ cm}^{-1}$  was set to YB for the area (integral value of  $1480\text{--}1680\text{ cm}^{-1}$ ) of peak PA near  $1580\text{ cm}^{-1}$  and value  $G=YA/YB$  of the surface ratio was measured.

[0069] (3) A tap density granular material density tool (Seishin Enterprise tap Densa KYT-3000) is used. The screen of 300 micrometers of openings was used as a screen which the carbon material for electrodes penetrates after dropping the granular material in the tap cell of  $20\text{ cm}^3$  and filling it up with a cell to the limit 10 mm of stroke length's tap was performed 1000 times and the tap density at that time was measured.

(4) 0.1% of true density surface-active agent solution was used and it measured with the

liquid phase substitution method by a pycnometer.

(5) After heating at 350 °C for predrying and passing nitrogen gas for 15 minutes using AMS-8000 by BET specific surface area Ohkuraiken CO.LTD.it measured by the one BET method by nitrogen gas adsorption.

(6) The 2 volume % solution (about 1 ml) of polyoxyethylene (20) sorbitan monolaurate which is a mean-particle-diameter surface-active agent is mixed to the carbon material for electrodes. The mean particle diameter (median size) of the volume reference was measured by making ion exchange water into carrier fluid with the laser diffraction type particle-size-distribution plan (LA-700 by Horiba Ltd.).

[0070](7) The mean circle form degree flow type particle image analysis apparatus (FPIA-2000 by TOA Medical Electronics Co.Ltd.) was used and measurement of the particle size distribution by a projected area diameter and calculation of circularity were performed. Ion exchange water was used as carrier fluid and polyoxyethylene (20) sorbitan monolaurate was used as a surface-active agent. With a projected area diameter it is a diameter of a circle (considerable circle) which has the same project area with the picturized particle image and circularity is the ratio which made the denominator the boundary length of the particle projection image which used the boundary length of the considerable circle as the numerator and was picturized. The circularity of all the measured particles was averaged and it was considered as the degree of mean circle form.

[0071](8) It asked for the coverage of the coverage multiple layer structure carbon material of a multiple layer structure carbon material from the following formula.  
[Mathematical formula 3] Coverage (weight %) =  $\ln a 100 - (K \times D) / (N \times (K + T)) \times 100$  top type As for K the weight (kg) of a carbon material and T express the weight (kg) of petroleum system tar D expresses the weight (kg) before detarring processing (the 2nd process) of kneaded material and N expresses the recovery amount (kg) of the thermally treated material after heat treatment (the 3rd process).

[0072](Embodiment 3) Half-\*\*\*\* was created using the prepared carbon material and charge/discharge capability was examined.

(1) What added the dimethylacetamide solution of polyvinylidene fluoride (PVdF) to the creation carbon material 5g of the half cell 10 weight % by solid content conversion was agitated and the slurry was obtained. This slurry was applied on copper foil with the doctor blade method and predrying was performed at 80 °C. After carrying out a consolidation with a roll press machine so that electrode density may furthermore become 1.4g/cm<sup>3</sup> or 1.5 g/cm<sup>3</sup> it pierced to discoid 12.5 mm in diameter reduced pressure drying was carried out at 110 °C and it was considered as the electrode. After an appropriate time after an appropriate time the coin cell which the electrode and the lithium metal electrode were made to counter focusing on the separator which made the electrolysis solution impregnate was created and the charge and discharge test was done. As an electrolysis solution what dissolved lithium perchlorate in the solvent which mixed ethylene carbonate and diethyl carbonate by the ratio of the weight ratio 2:8 at a rate of 1.5 mol/l. was used.

[0073](2) It charges to 0V by measuring electric-current density 0.16 mA/cm<sup>2</sup> of irreversible capacity (lithium ion dope to an electrode). Subsequently the value which subtracted the first service capacity from the first charging capacity at the time of making it discharge to 1.5V by current density 0.33 mA/cm<sup>2</sup> (lithium ion dedope from an electrode) was made into irreversible capacity.

(3) The charge to 0V in measuring-electric-current density  $0.16 \text{ mA/cm}^2$  of service capacity and discharge rate property (quick discharge characteristics) and discharge to 1.5V in current density  $0.33 \text{ mA/cm}^2$  were repeated 3 times and 3rd service capacity in that case was made into "service capacity." Charge to 0V by current density  $0.16 \text{ mA/cm}^2$  and discharge respectively Next current density  $2.8 \text{ mA/cm}^2$  Capacity obtained by carrying out to 1.5V by  $5.0 \text{ mA/cm}^2$  was made into the service capacity in each current density  $2.8 \text{ mA/cm}^2$  and  $5.0 \text{ mA/cm}^2$  and it was considered as the index of quick discharge characteristics. These test results are collectively shown in following Table 4.

[0074]

[Table 4]

[0075](Embodiment 4) Use carbon material No.11 for electrodes prepared in Embodiment 1 and the Seishin Enterprise pneumatic elutriation machine "MC-100" is used 25 weight % of fines and 22 weight % of coarse powder are classified on the conditions removed respectively Mean particle diameter after classification = 20.8 micrometers  $d_{02} = 0.336 \text{ nm}$  BET specific surface area =  $5.3 \text{ m}^2/\text{g}$  The carbon material for electrodes which has the physical properties of tap density =  $0.82 \text{ g/cm}^3$   $L_c > 100 \text{ nm}$  and true density =  $2.26 \text{ g/cm}^3$  and Raman R value = 0.25 and Raman 1580 half-breadth =  $22.0 \text{ cm}^{-1}$  was obtained. Subsequently except having used this carbon material for electrodes it experimented like Embodiment 2 and the multiple layer structure carbon material for electrodes which has the following physical properties was obtained. Raman R value = 0.37 Raman 1580 half-breadth =  $29.5 \text{ cm}^{-1}$  tap density =  $0.99 \text{ g/cm}^3$  BET specific surface area =  $2.3 \text{ m}^2/\text{g}$  mean-particle-diameter = 24.6 micrometer coverage = 4.9 weight %. Except having used the multiple layer structure carbon material obtained above the half cell was created like Embodiment 3 and charge/discharge capability was examined. As a result electrode density =  $1.5 \text{ g/cm}^3$  first time irreversible capacity =  $17 \text{ mAh/g}$   $0.33 \text{ A/cm}^2$  service capacity =  $352 \text{ mAh/g}$   $2.8 \text{ mA/cm}^2$  quick discharge capacity =  $351 \text{ mAh/g}$   $5.0 \text{ mA/cm}^2$  quick discharge capacity =  $334 \text{ mAh/g}$  and the good characteristic were shown.

[0076]

[Effect of the Invention] It has the feature that the cell using the carbon material for electrodes of this invention or the multiple layer structure carbon material for electrodes has large capacity ( $0.33 \text{ mA/cm}^2$  service capacity) the irreversible capacity accepted in an initial cycle is small and the capacity maintenance rate of a cycle is excellent. Further especially quick charge/discharge capability and ( $5.0 \text{ mA/cm}^2$  quick discharge capacity) are improved greatly. The discharge characteristic [ in / highly / for the preservability and reliability of a cell when it is neglected under an elevated temperature / low temperature ] is also excellent. Therefore the carbon material for electrodes and multiple layer structure carbon material of this invention can be used effective in manufacture of cells including a lithium cell.